

Enhanced catalytic ozonation inactivation of bioaerosols by MnO₂/Ni foam with abundant oxygen vacancies and O₃ at atmospheric concentration

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ABSTRACT

Catalytic ozonation is a promising bioaerosol control technology, as O₃ is prevalent in atmosphere. However, O₃ at atmosphere concentration has limited oxidation potential and reactive oxygen species (ROSs) production, leading incomplete bioaerosol inactivation. Therefore, a catalytic ozonation system with a manganese dioxide/Ni foam (MN) was prepared for efficient bioaerosol inactivation. The MN exhibited superior activity in catalytic ozonation bioaerosol inactivation, achieving 91.6% inactivation efficiency within 8.07 s at atmospheric concentration (0.1 ppm) of O₃. The inactivation efficiency can be further improved to 99.0% by regulating surface oxygen vacancies (O_v) in MN, which is mainly attributed to abundant O_v of MN that facilitate rapid conversion of O₃ to other ROSs. Meanwhile, the mechanism of rapid bacterial inactivation was also clarified at cellular level, showing that ROSs caused bacterial oxidative stress. This catalytic ozonation strategy would offer more choices to design efficient O₃ catalysts for bioaerosol control and public health protection.

1. Introduction

Bioaerosols have become one of the major air pollutants in modern society [1–3]. Long-term exposure to bioaerosols can cause severe cardiovascular, respiratory, and cardiopulmonary diseases [4–6]. In addition, the fast spread of bioaerosols is responsible for the outbreaks of various major public health events including severe acute respiratory syndrome (SARS) [7], Ebola virus disease (EVD) [8], and severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) [9]. In this context, many technologies including chemical methods (e.g., ClO₂, CH₃COOOH [10,11], photocatalytic inactivation [12,13]) and physical methods [14–16] (e.g., filtration and electrostatic adsorption) have been adopted to bioaerosol control. However, these technologies show some drawbacks. Chemical spraying is toxic to human respiratory system when people occupied. Photocatalytic inactivation involves harmful UV light, while filtration and electrostatic may cause secondary contamination. Therefore, it is of great necessity to develop a bioaerosol control strategy that can realize highly efficient inactivation without harmful

byproducts.

Ozone (O₃), with the advantages of no blind corners and no disinfection by-products, is very promising for the inactivation of bioaerosols [17], which is also prevalent in the environment with concentration of ~0.1 ppm at atmosphere [18]. O₃ inactivates bacteria mainly through oxidation by damaging the lipids of bacterial cell membranes, organelles, DNA, and RNA, which requires high concentrations due to limited oxidation potential of O₃ (2.07 eV) [19–22]. Exposure of high concentrations of O₃ is harmful to both humans and the environment [23,24], which cannot be applied to human occupied spaces [25]. On the other hand, O₃ at atmosphere concentration has less reactive oxygen species (ROSs) production, which may cause incomplete inactivation of bioaerosols and still pose a health exposure risk, thus inactivation efficiency of O₃ at atmosphere concentration should be enhanced.

Catalytic ozonation technology (O₃ oxidation in the presence of a catalyst) is an attractive option to enhance transformation of O₃ into atomic oxygen and to further evolve into ROSs for improving inactivation efficiency at the low concentration of O₃ [26,27]. Greater oxidation

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potential of ROSs (e.g. $\bullet\text{OH}$, 2.78 eV) in catalytic ozonation endows it higher inactivation efficiency and the less O_3 consumption [26]. To date, noble metal-containing catalysts such as Pd [28], Au [29], and Ag [30] are efficient catalysts for catalytic ozonation. However, the high cost and relative scarcity of noble metals limit the large-scale application of such catalysts. In this context, various non-noble metal O_3 catalysts like earth-abundant transition metals and their oxides have been designed and synthesized [31]. Among them, manganese dioxide (MnO_2) can be regarded as one of the most promising candidates due to its low cost and abundant on earth [32,33]. MnO_2 is always a reliable catalyst for efficient catalytic ozonation of odor methyl mercaptan [34] and bisphenol A [35]. In addition, MnO_2 with oxygen vacancies (O_V) is widely studied and applied for the ozone decomposition of volatile organic compound (VOC) ozonation [36,37], as O_V is considered to be the primary active site in the catalytic ozonation process. O_V in the MnO_2 enhances transformation of O_3 into atomic oxygen and further evolves into ROSs for potentially improving inactivation efficiency. However, bulky MnO_2 cannot be used for bioaerosol inactivation due to insufficient catalytic efficiency and easy fall off when exposed to the high air flow, resulting in catalysts loss [38]. Growing MnO_2 on nickel foam (NF) seems to be a promising strategy, because NF can act as a support that providing desirable three-dimensional (3D) open-pore structures and high specific surface areas for MnO_2 loading. Moreover, the 3D structure of NF also can be used as a microreactor to provide a space for sufficient contact between bioaerosols and ROSs.

Thereby, this study aimed to construct the MnO_2 sheets on nickel foam (MN) with abundant O_V for enhanced catalytic ozonation inactivation of bioaerosols and to understand the mechanisms involved in. MnO_2 catalyst was anchored on the surface of NF via a simple hydrothermal reduction method. The bioaerosol inactivation efficiency of the MN catalytic ozonation at atmospheric concentration of O_3 was investigated. Meanwhile, the catalytic mechanism was revealed by analyzing the phase compositions, surface chemical state, and redox abilities of MN. To illustrate deeply, the proposed inactivation mechanism was also verified at the cellular level by monitoring bacterial oxidative stress and membrane damage. This study may provide some basic information for the application of catalytic ozonation technology with low concentration of O_3 in reducing the risk of bioaerosol exposure.

2. Experimental section

2.1. Materials and reagents

NF with thickness of 3.0 mm was purchased from Guangzhou Lige Technology Co., LTD. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ($\geq 99\%$), KMnO_4 ($\geq 99\%$), HCl (36% – 38%), CH_3COOH ($\geq 99.5\%$), CH_3COCH_3 ($\geq 99.5\%$), nutrient broth, and nutrient agar were purchased from Aladdin Co. Ltd. DCFH-DA fluorescent probe was purchased from Beyotime Biotechnology Co. Ltd. All chemicals and reagents were used as received without any treatment.

2.2. Catalyst synthesis and characterization

Synthesis of MN: MN was prepared by a simple one-step hydrothermal reduction method. Firstly, NF pieces of $2.5\text{ cm} \times 2.5\text{ cm}$ were successively immersed in an ultrasonic bath of CH_3COCH_3 , 1 M HCl, and deionized H_2O for 30 min to remove stains and surface oxides, respectively. Then, the cleaned NF was quickly placed in a 100 mL Teflon-lined autoclave. Secondly, a mixed solution of 0.2 mM KMnO_4 and 0.1 mM $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in 80 mL deionized H_2O was slowly added into the autoclave. After 15 min of ultrasonic mixing, the Teflon-lined autoclave was transferred into an oven at 180°C for 12 h. Finally, the obtained MnO_2/NF (denoted as MN) was washed with deionized H_2O to remove soluble Mn salts, and dried at 60°C for 12 h.

Synthesis of MNE_x : MNE_x samples were prepared by hydrothermal treatment of MN different concentration of ethanol solution ranging

from 0%–50%. In detail, the MN obtained from hydrothermal treatment was then quickly placed in a 100 mL Teflon liner containing 80 mL different concentration of ethanol. The reaction temperature and time were 130°C and 12 h, respectively. The obtained samples (denoted as MNE_0 , $\text{MNE}_{0.25}$ and $\text{MNE}_{0.5}$) were dried at 60°C for 24 h.

Characterization: Scanning electron microscopy (SEM) observations were performed on Hitachi S-3400 N at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained by JEOL JEM-2100 microscope at an accelerating voltage of 200 kV. The surface morphology of the sample was measured by an atomic force microscopy (AFM) (Bruker Dimension Icon). The crystalline structure of the samples was characterized by an X-ray diffractometer (XRD) (Rigaku Ultima IV) using Cu-K α radiation. Raman spectra of the samples were obtained by Laser Micro-Raman Spectrometer (Horiba Scientific-LabRAM HR evolution, 514 nm laser). X-ray photoelectron spectroscopy (XPS) (Thermo Fisher ESCALAB 250Xi) was used to evaluate the bonding environment and oxidation state of surface elements (ca. 10 nm) on the catalysts. The formula used to estimate the average oxidation state (AOS) is $\text{AOS} = 8.956 - 1.126 \Delta\text{E}$ (ΔE is the difference in the binding energy between two peaks) [39]. The generated $\bullet\text{OH}$, $\bullet\text{O}_2$ and $^1\text{O}_2$ were detected by electron paramagnetic resonance (EPR) spectrometer (Bruker A-300, www.ece-shi.com). 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-112 piperidinol (TEMP) were used as the spin trapping reagents. In detail, 0.1 g catalysts were dispersed in a 100 mM DMPO/TEMP solution (2 mL) and then O_3 (0.1 ppm) was purged for 10 min. Finally, catalysts were filtered and the solvent was H_2O trapping $\bullet\text{OH}$ and $^1\text{O}_2$ and dimethyl sulfoxide (DMSO) for $\bullet\text{O}_2$. The ROSs generated on the catalysts in air were estimated by chemiluminescence. Luminol (100 μM) was employed as the indicator. Firstly, MN catalyst was exposed to O_3 flow for 10 min (catalytic O_3 reaction). After that, 100 μL luminol was dropped on the surface of the catalysts, immediately. The chemiluminescence of the luminol was detected by microplate reader (Varioskan LUX, ThermoFisher, USA) at the same time.

2.3. Catalytic ozonation bioaerosol inactivation experiment

Bioaerosol generation: Firstly, the experimental strain *E. coli* DH5 α was inoculated in a Luria-Bertani (LB) broth at 37°C . After about 12 h of shaking incubation, a bacterial suspension with a concentration of approximately 10^9 CFU mL^{-1} was obtained. Then, the above bacterial suspension was centrifuged at 8000 rpm for 2 min and resuspended in 0.9% NaCl solution. After washing twice with 0.9% NaCl solution, the above bacterial suspension was poured in a Collision six-jet nebulizer (BGI Inc., Waltham, MA) for bioaerosol generation. Then, the bioaerosols were injected and balanced in a chamber with a volume of 50 L. The concentration of bioaerosols was adjusted by the concentration of bacterial stock suspension. The particle size of generated bioaerosols is approximately $1 - 3\text{ }\mu\text{m}$ (Fig. S1).

Bioaerosol sampling: In this study, liquid sampler and an Anderson six-stage sampler were used to collect the bioaerosols from the reactor. The sampling medium of liquid sampler was 10 mL of 0.9% NaCl solution. The sampling flow rate of the liquid sampler was $7 - 12.5\text{ L min}^{-1}$. The sampling flow rate of the Anderson six-stage sampler was 28.3 L min^{-1} . The sampling air volume was adjusted to 50 L. The collected samples (100 μL) were diluted and cultured on a nutrient agar plate at 37°C for 18 – 24 h.

2.3.1. Evaluation of bioaerosol inactivation performance of MN catalytic ozonation

The experimental setup for bioaerosol inactivation by MN catalytic ozonation was shown in Fig. S2. In detail, the MN was sealed in the middle of the quartz reactor, which connected to the outlet of the balance chamber. An O_3 generator (FQ-160, Beyok, China) was used to generate O_3 at a concentration of 0.1 ppm, 1 ppm, and 5 ppm. During the inactivation reaction, the bioaerosols and O_3 passed through the MN from the top to the bottom of the quartz reactor. At last, the bioaerosols

were collected by the bioaerosol sampler from the outlet of the quartz reactor. Meanwhile, the concentration of O_3 in the reactor was monitored online using a O_3 sensor (RS485, Vemsee, China). The detailed parameters of the bioaerosol inactivation experiment were shown in Table S1. The inactivation efficiency (η) was calculated using the following Eq. 1:

$$\eta = \left(1 - \frac{C}{C_0}\right) \quad (1)$$

C_0 (CFU m^{-3}) is the concentration of initial bioaerosols; C (CFU m^{-3}) is the concentration of bioaerosols after catalytic ozonation inactivation.

2.4. Cellular assay

Bacterial oxidative stress response: Bacterial oxidative stress response was monitored by the fluorescent probe DCFH-DA (Beyotime Biotechnology), and the detailed operation is shown in the Supporting information (SI).

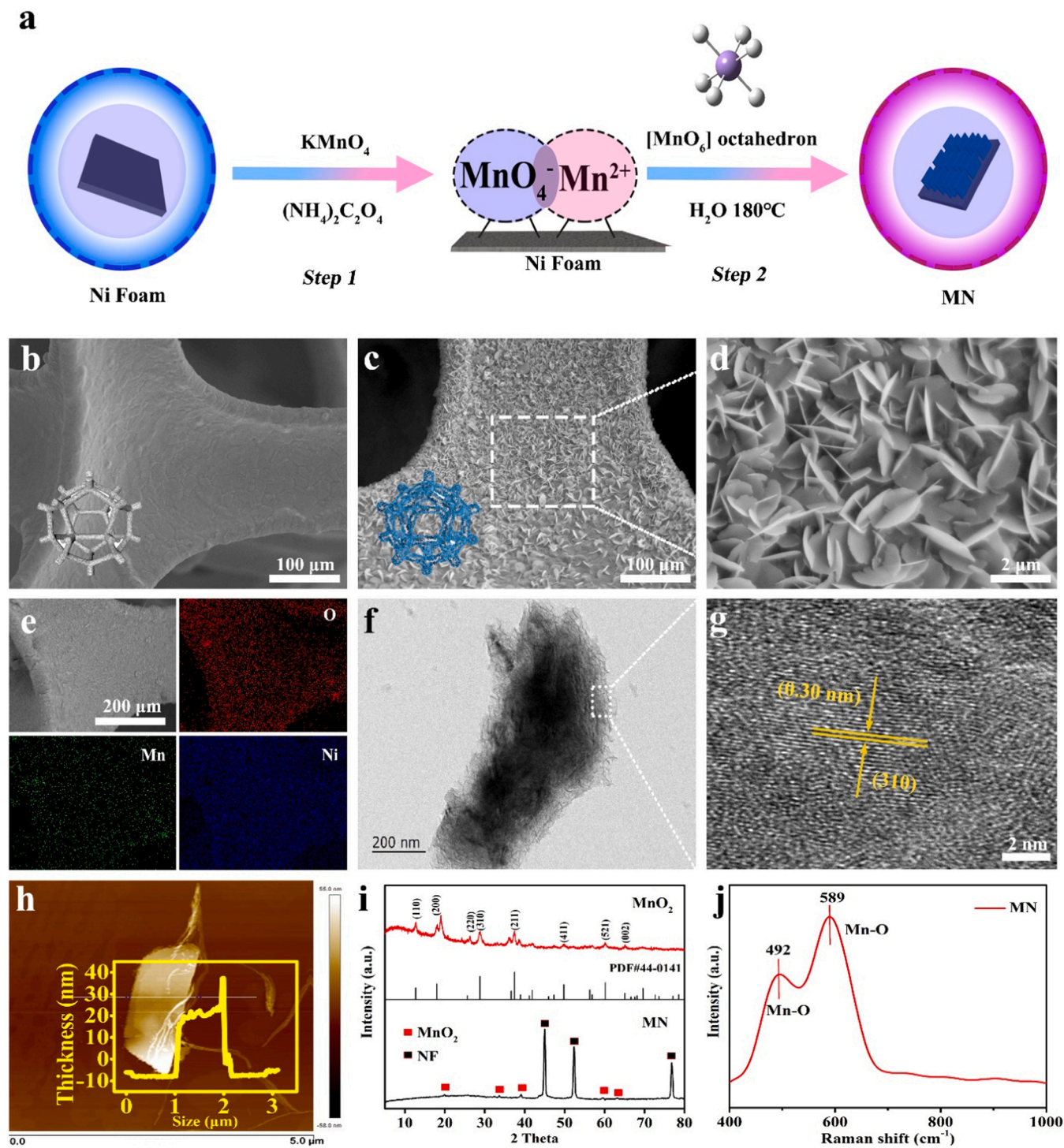


Fig. 1. a) Illustration of synthesis procedure of MnO_2 onto NF. SEM images of b) bare NF, MN c) at low magnification and d) at high magnification; e) EDS elemental mapping images of MN; TEM images of MN f) at low magnification and g) at high magnification; h) AFM images of MN; i) XRD patterns of MN and MnO_2 powder, and j) Raman patterns of MN.

Bacterial adenosine triphosphate: The adenosine triphosphate (ATP) was measured using a detection kit (Beyotime Biotechnology, China), and the detailed operation is shown in SI.

Bacterial morphology: The morphology of the bacteria was observed by SEM at an accelerating voltage of 5 kV. The detailed preparation steps of SEM samples are also provided in SI.

3. Results and discussion

3.1. Morphology and structure characterization of MN

The synthesis process of MnO_2 on the surface of NF by a facile hydrothermal treatment is schematically illustrated in Fig. 1a. KMnO_4 undergoes a redox reaction with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution to form MnO_2 at 180°C . The chemical reactions can be formulated as two reactions: $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ = 10\text{CO}_2\uparrow + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ (1); $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} = 4\text{H}^+ + 5\text{MnO}_2\downarrow$ (2) [40]. When the clean NF is immersed in the mixture of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and KMnO_4 solution, the $[\text{MnO}_6]$ octahedron unit (the basic structural units for MnO_2) is firstly formed on the surface of NF by bonding with oxygen atoms of oxygen-containing functional groups via electrostatic force. In the subsequent hydrothermal process, the $[\text{MnO}_6]$ octahedron unit grows into MnO_2 on the surface of NF.

The morphology and microstructure of MN were systematically analyzed. The SEM images in Fig. 1c shows that the MnO_2 was successfully anchored onto the smooth surface of the NF (Fig. 1b) after 12 h of hydrothermal treatment. The SEM image at high magnification (Fig. 1d) and energy-dispersive X-ray (EDS) mapping (Fig. 1e) of MN also confirm successful and uniform growth of MnO_2 nanosheets onto NF. The microstructure of the MnO_2 sample was further observed via peeling MnO_2 nanosheets from the surface of NF, showing square-sheet shape with size of $2\text{ }\mu\text{m}$ (Fig. 1f). The detailed analysis of HRTEM images (Fig. 1g) reveals that the lattice space of MnO_2 nanosheets is 0.30 nm ,

corresponding to the (310) plane of MnO_2 . In addition, the AFM image indicates that the MnO_2 nanosheets anchored onto the surface of NF are very thin and the thickness is only about 20 nm (Fig. 1h). XRD pattern of MnO_2 peeling from NF displayed in Fig. 1i shows distinct peaks at 12.8° , 18.1° , 25.7° , 28.9° , 37.6° , 49.9° , 60.2° , and 65.1° , corresponding to the diffraction plane of (110), (200), (220), (310), (211), (411), (521), and (002), respectively (PDF 44 – 0141) [34]. The peaks of MN located at 44.9° , 52.3° and 76.7° could be ascribed to the (111), (200), and (220) planes of Ni foam (PDF# 04–0850) [41]. The molecular arrangement structure of MN also analyzed by a Raman spectrometer (Fig. 1j). Two peaks located at 492 and 589 cm^{-1} are derived from the stretching vibration of the Mn-O bond in $[\text{MnO}_6]$ sheet basal planes and the Mn-O symmetric stretching vibration along the direction perpendicular to $[\text{MnO}_6]$ groups [42,43]. In short, the above characterization results verify the successful growth of sheet-like MnO_2 onto the surface of NF.

3.2. Evaluation of catalytic ozonation inactivation efficiency of bioaerosols onto prepared catalyst

The MN catalyst was assembled in a quartz reactor for catalytic ozonation bioaerosol inactivation tests. The bioaerosol inactivation efficiency was estimated by the standard plate counting method of bacteria. In order to obtain convective bioaerosol inactivation efficiency in catalytic ozonation system of MN/O_3 , the inactivation performance of O_3 , NF, O_3/NF , MN, and MN/O_3 systems were comparatively investigated. Here, 0.1 ppm concentration of O_3 (an average atmospheric concentration) was chosen for catalytic ozonation reaction. As displayed in Fig. 2a, the bioaerosol inactivation efficiency of O_3 alone (0.1 ppm) is only 1.9% at the retention time of 8.07 s , indicating that at an atmospheric concentration of O_3 is not able to significantly inactivate bacteria in such a short time. Meanwhile, the similar low bioaerosol inactivation efficiency of only 9.8% with NF alone was found, suggesting that the NF is not effective in removing bioaerosols, either. For NF/O_3

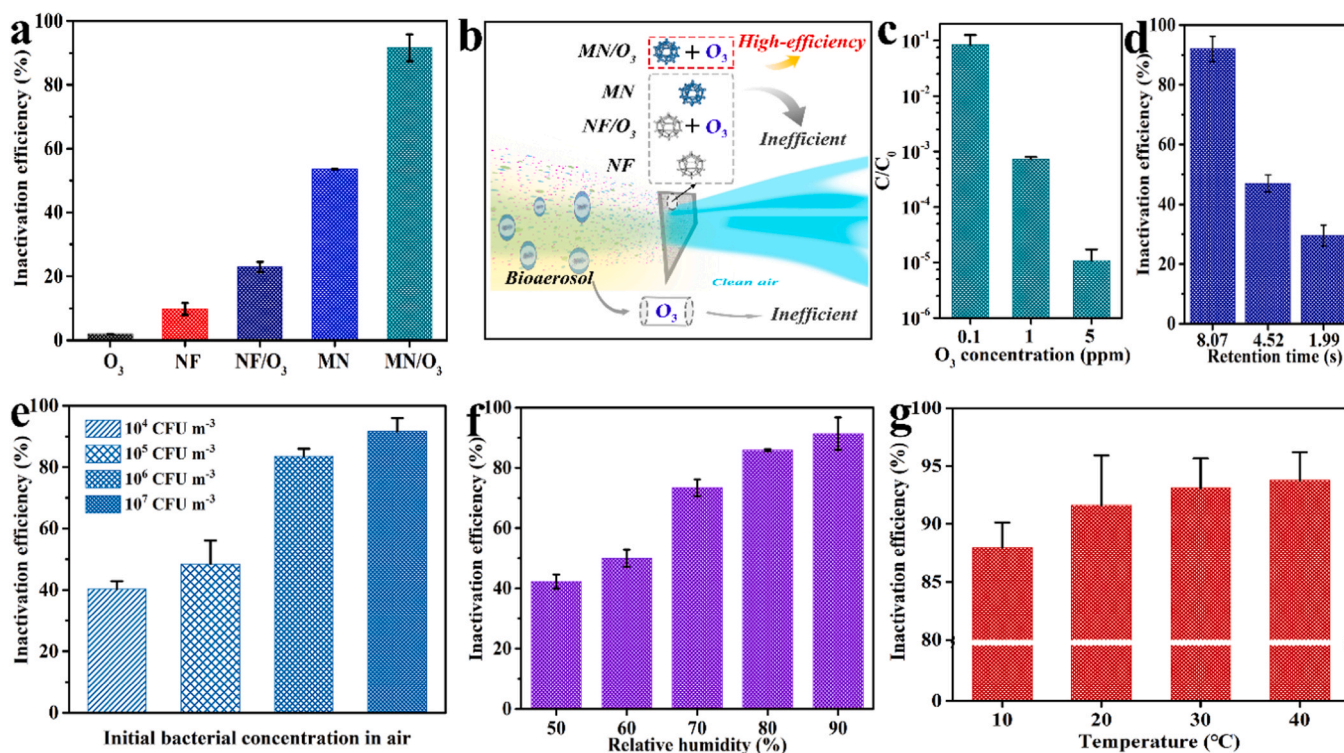


Fig. 2. a) Comparison of the bioaerosol inactivation efficiency of O_3 , NF, NF/O_3 , MN, and MN/O_3 ($\text{RH} = 90\%$, retention time = 8.07 s), respectively; b) Illustration of the bioaerosol inactivation efficiency of O_3 , NF, NF/O_3 , MN, and MN/O_3 , respectively; c) Effect of concentration of O_3 on the bioaerosol inactivation efficiency. d) Effect of retention time on bioaerosol inactivation efficiency ($\text{RH} = 90\%$). e) Effect of concentration of bacteria on bioaerosol inactivation efficiency; f) Effect of relative humidity on bioaerosol inactivation efficiency (retention time = 8.07 s); g) Effect of temperature on bioaerosol inactivation efficiency.

and MN systems, the bioaerosol inactivation efficiency were also obtained as 22.9% and 53.6%, respectively. MN catalyst shows higher inactivation efficiency than NF/O₃, which can partly inactivate a portion of bioaerosols. However, in MN/O₃ system, the inactivation efficiency of bioaerosols is obtained as 91.6%, which is much higher than that of O₃, NF/O₃ and MN. As illustrated in Fig. 2b, the inactivation efficiency of MN/O₃ system is significantly higher than other three systems, maybe attributed to that MnO₂ can catalyze O₃ at an atmospheric concentration (0.1 ppm) to produce high oxidation potential of ROSs and some physical damages by MnO₂ nanosheets for bioaerosol inactivation at a short time [44]. In MN system without O₃, no catalytic oxidation involved, the limited inactivation efficiency of bioaerosols may attribute to physical damage by MnO₂ nanosheets, based on our previous study [41]. Furthermore, the low inactivation efficiency of NF/O₃ probably owns to lacks of not only catalytic oxidation but also physical damage. Even though O₃ possesses oxidation potential to inactivate bioaerosols, the efficiency of it is limited at such a low concentration and short retention time. However, in the MN/O₃ system, enhanced catalytic oxidation was achieved by reaction between MN catalyst and O₃, resulting in high inactivation efficiency of bioaerosols.

In order to explore the performance of the MN/O₃ system for practical application, the impacts of concentration of O₃, retention time, concentration of bioaerosols, environmental temperature and relative humidity on the catalytic ozonation inactivation efficiency of bioaerosols in MN/O₃ system were investigated. Firstly, increasing the concentration of O₃ can significantly improve bioaerosol inactivation efficiency of the MN/O₃ system. With the concentration of O₃ increases from 0.1 to 1 and then to 5.0 ppm, the bacteria reduction improves significantly (from 1 log to ~2 log and then to 4 log) (Fig. 2c). These results highlight the excellent catalytic ozonation performance of MN to some extent to O₃ even at atmospheric concentrations (0.1 ppm). However, the usage of high concentration of O₃ (1 and 5 ppm) to inactivate indoor bacteria is still in debate, because exposure of high concentrations of O₃ is harmful to both humans and the environment [45]. Thus, to balance the catalytic ozonation inactivation efficiency with O₃ exposure risks for catalytic ozonation inactivation of bioaerosols in the enclosed spaces, 0.1 ppm of O₃ was therefore selected for the following MN/O₃ catalytic inactivation experiments.

The retention time is of great importance in the practical application of this efficient technology. As plotted in Fig. 2d, the long retention time has positive influence on the catalytic ozonation inactivation efficiency of bioaerosols. The inactivation efficiency is only 29.5% at a short retention time of 1.99 s, and then increases to 47.1% at a retention time of 4.52 s. With the retention time extended to 8.07 s, the inactivation efficiency of bioaerosols reaches up to 91.6%. The high inactivation efficiency at long retention time can be easily explained by the fact that bioaerosols have more chances to interact with produced ROSs, yielding the improved inactivation efficiency. However, it does not mean an endless extension of the retention time for increasing inactivation efficiency, because long residence time causes the slow flow rates, resulting in low processing capacity per unit time (Table S1). The purification air volume and catalytic inactivation efficiency need to be reasonably balanced, thus an optimized retention time of 8.07 s was chosen in the following tests.

In atmospheric environment conditions, the concentration of bioaerosols varies greatly in different areas, ranging from ~10³ to ~10⁶ CFU m⁻³ [46–48]. Therefore, the catalytic ozonation inactivation efficiency of MN/O₃ system under different initial concentrations of bioaerosols (10⁷, 10⁶, 10⁵, and 10⁴ CFU m⁻³) was also explored. As depicted in Fig. 2e, the inactivation efficiency of bioaerosols obtained about 40.2% at concentration of 10⁴ CFU m⁻³. With the concentration of bioaerosols further increases from 10⁵ to 10⁶ CFU m⁻³, the inactivation efficiency improves from 48.4% to 83.5% and then reaches 91.6% at 10⁷ CFU m⁻³. It can be explained by that the holes size of NF (200–300 μm) is obviously larger than the particle size of generated bioaerosols (1–3 μm), such a structure makes it easy for bioaerosols to pass through

the holes of the NF with the airflow. When the concentration of bioaerosols increased, more cells approach the NF surface, which in turn are attacked by the ROSs generated on the surface of the catalyst, thus the inactivation efficiency was improved [49].

Furthermore, the catalytic ozonation inactivation efficiency of bioaerosols in MN/O₃ system was further measured under different relative humidity (RH) conditions. As presented in Fig. 2f, the inactivation efficiency is obtained as only 42.2% when the RH is 50% ± 3%, then increases to 50.1% and 73.4% at 60% ± 3% RH and 70% ± 3% RH, respectively. When the RH continuously increase to 80% ± 3%, the inactivation efficiency rises to 85.8% accordingly. The reason maybe that MN could catalyze the reaction of O₃ and OH⁻ in water vapors to produce H₂O₂ and then H₂O₂ is further converted to ROSs at high RH [50]. Thus, the high concentration of ROSs enhances the bioaerosol inactivation performance of MnO₂/O₃ at high RH. In addition, the cell membrane of bacteria may swell and become thin in high RH, resulting in easy inactivation of the bacteria [45]. These results show that the inactivation efficiency of bioaerosols in the MN/O₃ system is positively correlated with RH, indicating that the MN/O₃ system can adapt to humid environment for bioaerosol control.

Additionally, the inactivation efficiency of bioaerosols in MN/O₃ system at various ambient temperatures was also studied. It can be seen from Fig. 2g that the inactivation efficiency rises slowly with increase of ambient temperature. At low temperature (10 ± 5 °C), the inactivation efficiency is obtained as 87.9%, while reaches 91.6%–93.1% at the near standard ambient temperature range (20 ± 5 °C–30 ± 5 °C). As the temperature rises to 40 ± 5 °C, the inactivation efficiency increases to 93.7%. The reason maybe that high temperature causes the quick mass transfer of O₃ molecules during catalytic ozonation reactions [36]. All above results confirm that the MN/O₃ system possesses a high potential to bioaerosol control at different environmental conditions for practical applications.

3.3. Catalytic ozonation inactivation mechanism of bioaerosols

3.3.1. Exploration of the promoting effect of oxygen vacancies (O_V) and ROSs

To understand the underlying mechanisms of the high catalytic ozonation inactivation activity, the element valence states of MN surface were investigated [43]. The valence state of Mn element can influence the formation of O_V on MnO₂ to maintain charge balance and O_V always works as active site in the catalytic ozonation process [51]. To explore the promotion of O_V in catalytic ozonation inactivation activity, the surface features and the valence state of Mn element in MN after the reduction by different concentration of ethanol (introducing O_V in MnO₂, which leads to reduction of valence state of Mn element) were first analyzed. It can be seen from Fig. S3 that the Mn element valence state of MN changed significantly after being reduced by ethanol (MNE_{0.5}) and used for catalytic ozonation (used MNE_{0.5}). Mn 2p_{3/2} spectrum of MN can be divided into three peaks located at 640.6, 641.6, and 642.9 eV, which are corresponding to Mn²⁺, Mn³⁺, and Mn⁴⁺, respectively [52]. Peak area represents the percentage of different Mn element valence states. Existing low valence states (Mn²⁺ and Mn³⁺) of Mn indicates the formation of O_V [53]. The percentages of Mn²⁺ and Mn³⁺ increased while the percentage of Mn⁴⁺ decreased in MNE_{0.5} after ethanol treatment, indicating that the valence state of the MNE_{0.5} reduced and the amount of O_V increased. On the other hand, the percentages of Mn²⁺ and Mn³⁺ decreased while Mn⁴⁺ increased significantly in used MNE_{0.5}, which maybe due to the oxidation of Mn element by O₃ and occupation of O_V by absorbates. The AOS of surface Mn element is further estimated by the binding energy difference (ΔE) between the two peaks of Mn 3s (Fig. 3a). The calculated AOS for Mn element of MN is 3.32, and the Mn elements AOS of MNE_{0.5} is 2.65, indicating the Mn element valence state was decreased after ethanol reduction. However, the Mn elements AOS of used MNE_{0.5} increased to 3.10. These results fully manifest that the surface elements valence

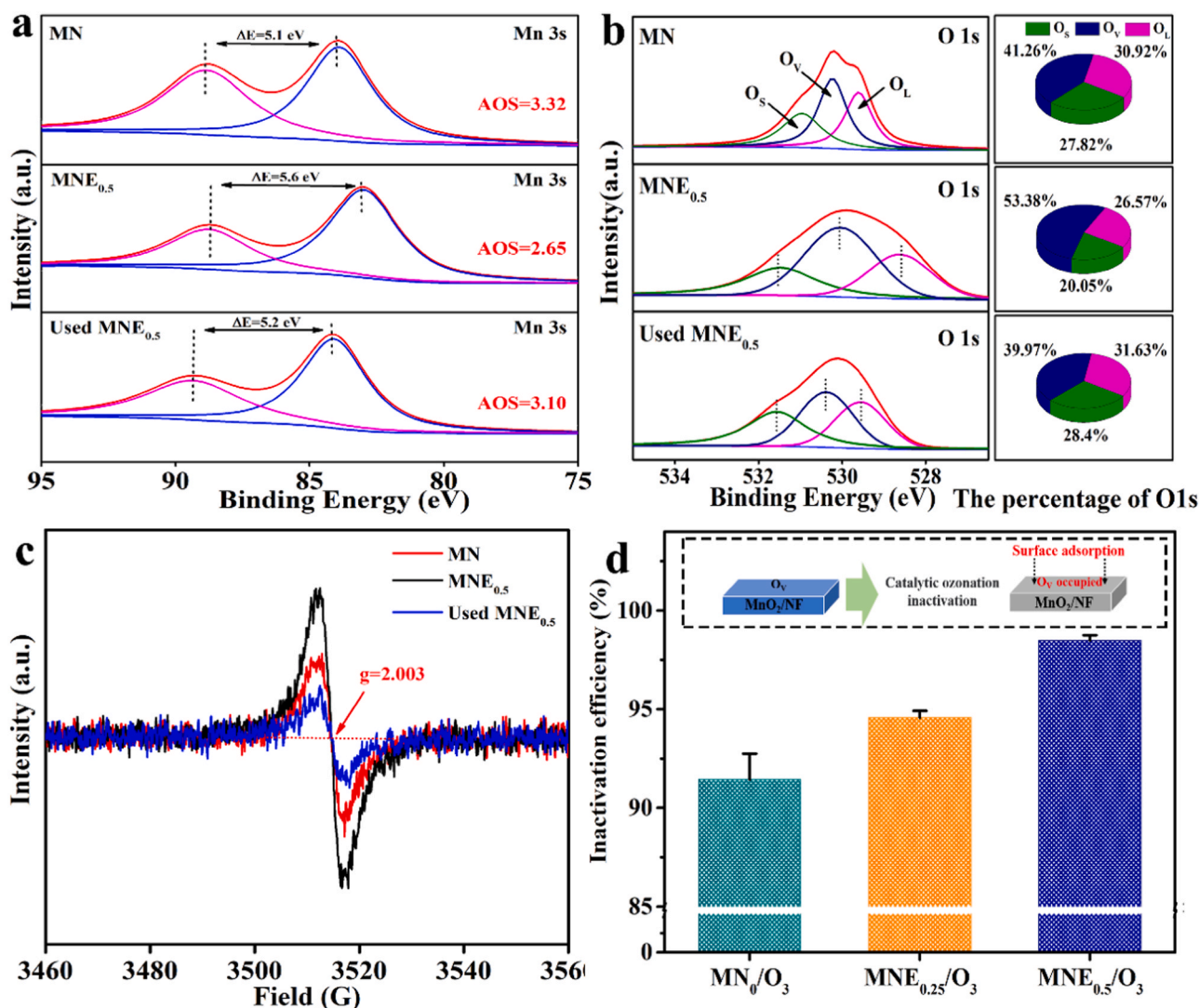


Fig. 3. XPS spectra of a) Mn 3s and b) O 1s of MN, MNE_{0.5} and used MNE_{0.5}; c) EPR spectra of MN, MNE_{0.5} and used MNE_{0.5}; d) Comparison of the bioaerosol inactivation efficiency of MN₀/O₃, MNE_{0.25}/O₃ and MNE_{0.5}/O₃ (RH = 90%, retention time = 8.07 s).

states of MN reduced after ethanol reduction and increased after catalytic ozonation reaction, indicating O_v in the MN was consumed after catalytic ozonation reaction.

To figure out if O_v is the key factor in catalytic ozonation inactivation efficiency, the O 1s spectra of the catalysts were analyzed immediately thereafter. The O 1s spectrum of MN in Fig. 3b is divided into three peaks located at 529.9, 531.5, and 533.3 eV, which are assigned to the lattice oxygen species (O_L), low-coordinated oxygen adsorbed in oxygen vacancies (O_v) such as O⁻, O²⁻, OH groups and surface residual hydroxyl molecules (O_s), respectively [54,55]. It is worth noting that the percentage of various oxygen species in MNE_{0.5} and used MNE_{0.5} are both changed obviously compare with MN. In particular, the percentage of O_v increases from 41.3% (MN) to 53.4% (MNE_{0.5}), which demonstrates that ethanol reduction method significantly increased the concentration of surface O_v. On the contrary, the percentage of O_v in used MNE_{0.5} decreases to 40.0%, which may cause by O_v occupation by surface adsorbates [56]. The high O_v concentration in MN was further verified by the EPR results (Fig. 3c), where the symmetric signal with a g-value at 2.003 contributed to the electrons trapped in the O_v [34]. In addition, the higher peak intensity means the higher concentration of the O_v in the catalyst. The peak intensity of MNE_{0.5} was higher than that of MN and used MNE_{0.5}, verifying that MNE_{0.5} has the highest concentration of O_v among the three catalysts, which is also consistent with the

XPS results. Moreover, survey spectra of MN, MNE_{0.5} and used MNE_{0.5} were also demonstrated in Fig. S4, indicating that the element composition of elements on the surface of the catalyst did not change before and after catalytic ozonation. In short, the above results indicate that the abundant surface O_v in MN is the active site in the catalytic ozonation process.

To explore the promoting effect of O_v in catalytic ozonation inactivation activity, the catalytic ozonation inactivation efficiency of MN after ethanol reduction were also evaluated. As displayed in Fig. 3d, the catalytic ozonation inactivation efficiency of MN₀/O₃, MNE_{0.25}/O₃ and MNE_{0.5}/O₃ were obtained as 92.0%, 94.6% and 99.0%, respectively, indicating that the catalytic ozonation inactivation efficiency increased with rise of O_v concentration in MN. Moreover, we also investigated the cycling test of MN/O₃ system. As shown in Fig. S5, the bioaerosol inactivation of MN/O₃ system gradually decreased for 4 times, which may be that the adsorbed H₂O molecule is hard to desorb from the surface O_v. Importantly, the morphology (Fig. S6), element components (Fig. S7) and structural features (Figs. S8 and S9) of MNE_{0.5} are similar to that of MN. Moreover, Figs. S10 and 2i show that XRD pattern of MNE_{0.5} powder is corresponding to MnOOH/MnO₂ heterojunction, indicating that some of the valence of Mn (+4) in MnO₂ has been reduced to Mn (+2). It was reported that the formation of heterojunction also contributes to the increase of O_v on the catalyst [57]. Consequently,

we can confirm that the key factor of the high catalytic ozonation inactivation activity of MN/O₃ system is the abundant O_V on the surface of MN.

O_V is beneficial to electron transfer to participate in the catalytic ozonation reaction and produce more ROSs such as •OH, •O₂⁻ and ¹O₂, which is critical for highly inactivation activity [58]. To confirm it, the ROSs (•OH, •O₂⁻ and ¹O₂) generation in catalytic ozonation was detected in liquid phase by EPR spectrometer. As shown in Fig. 4a, the characteristic peaks of •OH with the intensity of 1: 2: 2: 1 can be detected in all samples, while shows a higher intensity in MNE_{0.5}/O₃ system than that of MN/O₃ and used MNE_{0.5}/O₃ systems, indicating higher concentration of ROSs generation in MNE_{0.5}/O₃ system. This result indicates that MNE_{0.5}/O₃ possesses a stronger capability to generate •OH than other systems, which attributes to the low valence state of Mn in MNE_{0.5} system. Meanwhile, as shown in Figs. 4b and 4c, the concentration of •O₂⁻ and ¹O₂ in MNE_{0.5}/O₃ system were also higher than that of MN/O₃ system, while dropped significantly after being used. Moreover, we also detected the ROSs generated in air by chemiluminescence of luminol to confirm the results from EPR. As previously reported, luminol (100 μM) was employed as the indicator to reflect the generation of ROSs by chemiluminescence [59,60]. When luminol reacts with ROSs, it can generate blue fluorescence (~420 nm), which can be used to signal the generation of ROSs by the MN/O₃ system. Firstly, MN catalyst was exposed to O₃ flow for 10 min (catalytic O₃ reaction). After that, 100 μL luminol was dropped on the surface of the catalysts, immediately. The chemiluminescence of the luminol was detected by microplate reader at

the same time. We found that the characteristic peak at 420 nm of the MNE_{0.5} was the highest among MN, MNE_{0.5} and used MNE_{0.5} systems (Fig. 4d), indicating that the ROSs generation in MNE_{0.5} is the highest. These results not only confirm that ROSs were generated at the interface of the catalyst and air, but also show that the concentrations of ROSs are corresponding to the EPR results in the different systems. Therefore, we can firstly conclude that abundant O_V is beneficial to generate ROSs to inactivate bioaerosols.

In this study, we found that the O_V concentration in the MnO₂ catalyst has impacts on the performance of bioaerosol inactivation, which supported the oxygen vacancies theory among many theories (Table S2). Therefore, the possible mechanism of the ROSs generated from O_V in the MN/O₃ system could be summarized together with early references by the following reaction pathways [61–63]. Firstly, in the MN/O₃ system, O₃ can be captured by the O_V onto the surface of MN when O₃ go through MN. The O_V onto MnO₂ transfers two electrons to an oxygen atom of O₃ (two-electron donor), resulting in one O₂ molecule desorbing into the ambient air and one reactive oxygen (O₂⁻) remaining in the O_V (Eq. 2). Secondly, the other O₃ molecule can then react with the O₂⁻ in O_V to produce one O₂ molecule and a bridging O₂ dimer (peroxide, O₂²⁻) species (Eq. 3). At last, charge transfer interactions drive the reaction between O₂²⁻/O₂⁻ and O₃ to generate ROSs such as •OH, •O₂⁻ and ¹O₂ (Eq. 4 and Eq. 5). Simultaneously, to sustain the electrostatic balance, the O₂⁻ accumulated on surface of MN can be converted into O₂ molecules, releasing a part of O_V (Eq. 6).

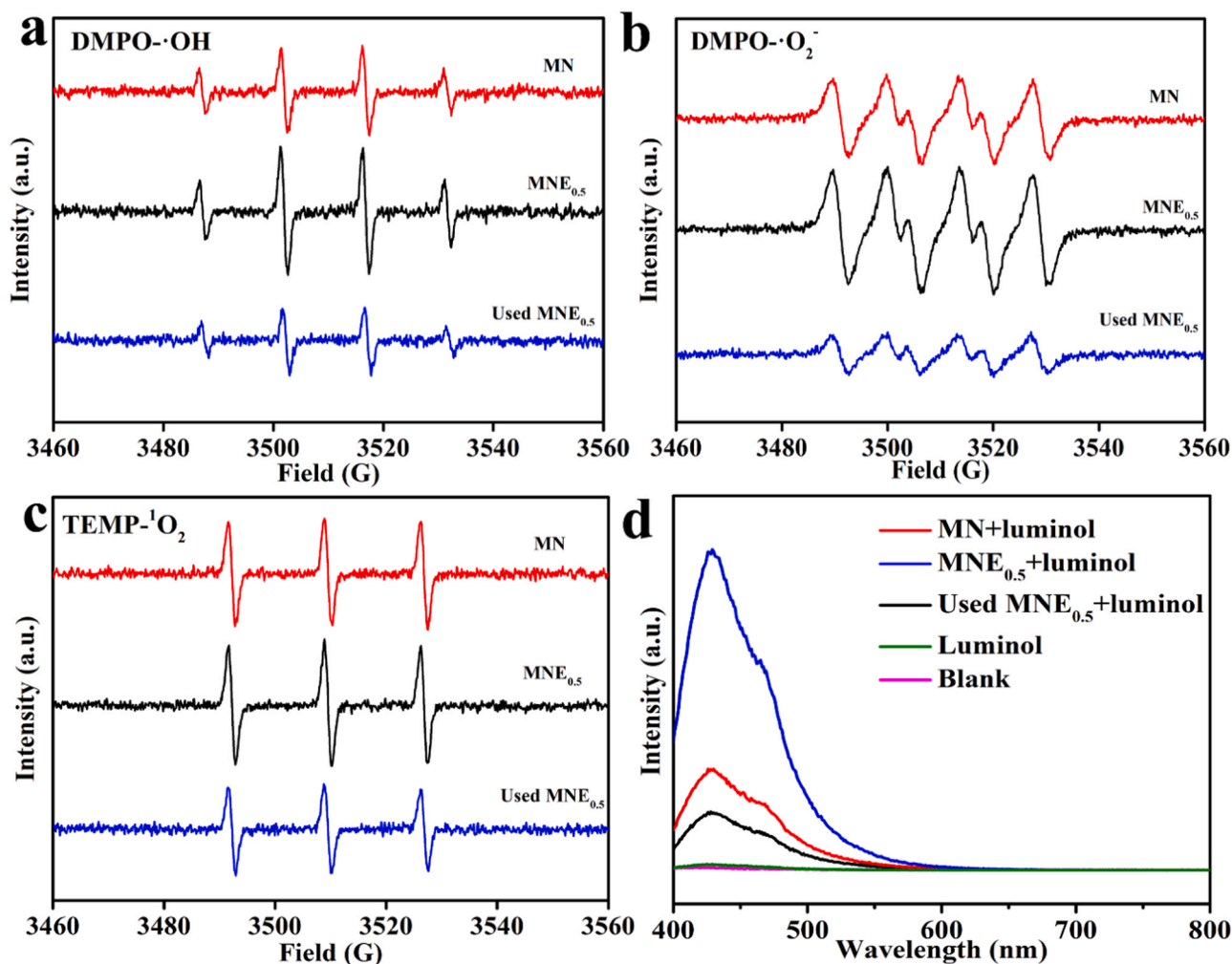


Fig. 4. Comparison of EPR spectra of MN, MNE_{0.5} and used MNE_{0.5}. a) •OH, b) •O₂⁻ and c) ¹O₂; d) Chemiluminescence spectra of luminol dropping on MN, MNE_{0.5} and used MNE_{0.5}.



Although there is lack of data support for the generation of atomic oxygen (O^-/O^{2-}) in the activation pathway of O_3 , it also can be considered that the exposure of more active sites (O_V) on the MN promotes the production of ROSs in the catalytic ozonation process, and thus improves the inactivation activity of bacteria in bioaerosols.

3.3.2. Exploration of the bacterial oxidative stress and damage in the MN/ O_3 system

In order to further understand the mechanism of the bacteria inactivation, the oxidative stress and morphology change of bacteria in the MN/ O_3 system were investigated. The oxidative stress is a self-defense response of bacteria when they suffer from external stimulation and one of the indicators of bacterial oxidative stress is intracellular ROSs production [64]. As displayed in Fig. 5a, the intracellular ROSs level of bacteria being treated in MN/ O_3 system is much higher than that of control system. This result indicates catalytic ozonation in the MN/ O_3 system can induce significant increase of intracellular ROSs levels of bacteria. Severe oxidative stress of bacteria may cause a decrease in cellular activity, which can be indicated by the ATP activity of bacteria. ATP activity of bacteria being treated in MN/ O_3 is much lower than that of without treatment, indicating that severe oxidative stress of bacteria caused by MN/ O_3 system reduce cellular activity obviously. Further, we found that morphology of bacteria changed after being treated in the MN/ O_3 system. As shown in Fig. 5b and c, the morphology of bacteria treated in the MN/ O_3 system was collapsed and shrunken, while that of untreated bacteria was complete with rod shape, indicating the damage of cell membrane of bacteria in the MN/ O_3 system. The inset picture of the Fig. 5b and c also show that the number of culturable bacteria in bioaerosols reduced significantly after being treating in the MN/ O_3 system. These results correspond to the results of oxidative stress and cellular activity of bacteria. Therefore, the bacteria in bioaerosols were under severe oxidative stress in the MN/ O_3 system, leading to reducing cellular activity, further cell membrane damage and cell inactivation in the end. It is worth noting that this severe oxidative stress response of bacteria comes from the external stimuli of high concentration of ROSs generated in the MN/ O_3 system. In this situation, not only intracellular ROSs from oxidative stress, but also extracellular ROSs from catalytic ozonation attack bacteria to destroy membrane structure and bacterial normal metabolic processes, yielding inactivation of them. It can be concluded that the high bioaerosol inactivation efficiency of the MN/ O_3 system attributes to the tremendous structural and physiologic damages

of bacteria.

3.3.3. Proposed inactivation mechanisms of the MN/ O_3 system

Hence, based on the results discussed above, the bioaerosol inactivation mechanism of the MN/ O_3 system was proposed. As shown in Fig. 6, O_3 molecules (atmospheric concentration) are firstly captured by the O_V (active sites) on the surface of MN catalyst (MnO_2 with abundant O_V were anchored on NF). The O_V transfers two electrons to O_3 , generating ROSs such as $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and ${}^1\text{O}_2$ in air. When the bacteria approaching the surface of MN, they can be attacked by the high concentration of ROSs. The bacteria will be under severe oxidative stress response to this external stimulate, yielding reduction of ATP activity. Finally, the intracellular ROSs that caused by oxidative stress and ROSs generated in the MN/ O_3 system can synergistically destroy bacterial membrane structure and normal metabolic processes of the bacteria, leading to inactivation of them. Therefore, in the MN/ O_3 system, O_V on the MnO_2 catalyzes low concentration of O_3 to highly active ROSs, yielding high bioaerosol inactivation efficiency within a short time.

4. Conclusions

The limitations of O_3 oxidation for bioaerosol inactivation are that the potential toxicity to humans at high concentrations, but poor efficiency at low concentrations owing to the limited oxidation potential. In this study, a novel catalytic ozonation strategy consisting of a MN catalyst coupled with O_3 was successfully proposed. The catalyst with abundant exposed active sites (O_V) exhibited an outstanding bioaerosol inactivation activity of 99.0% at 0.1 ppm of O_3 (atmospheric concentration). The MN catalyst with abundant O_V can convert low concentrations of O_3 into ROSs with high oxidation capacity to rapidly inactivate bioaerosols. Bacteria suffered from severe bacterial oxidative stress, cellular activity decrease and membrane damage in the MN/ O_3 system, yielding quick inactivation of bioaerosols. This work offers a highly efficient catalytic ozonation strategy for inactivation of bioaerosols, which can be a promising candidate for comprehensive and deep air purification in home, schools, vehicles, etc.

CRediT authorship contribution statement

Li Guiying: Writing – review & editing, Funding acquisition. **Liu Hongli:** Visualization, Investigation. **Liang Zhishu:** Validation, Methodology. **Zhao Huijun:** Validation. **Wang Haiyu:** Writing – original draft, Methodology, Formal analysis. **Peng Linghui:** Methodology, Data curation. **An Taicheng:** Supervision, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

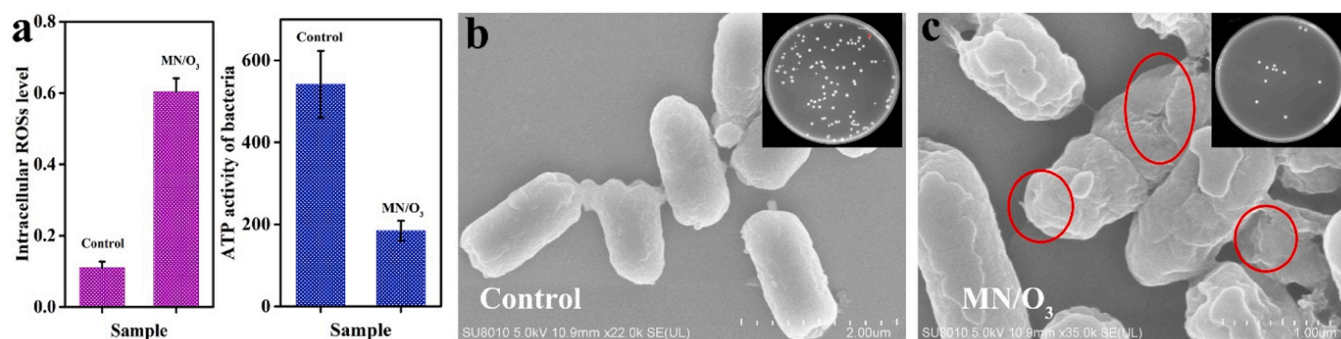


Fig. 5. a) The intracellular ROSs and ATP of bacteria without and after being inactivated with MN/ O_3 ; SEM images of bacteria after being inactivated b) without, and c) with MN/ O_3 .

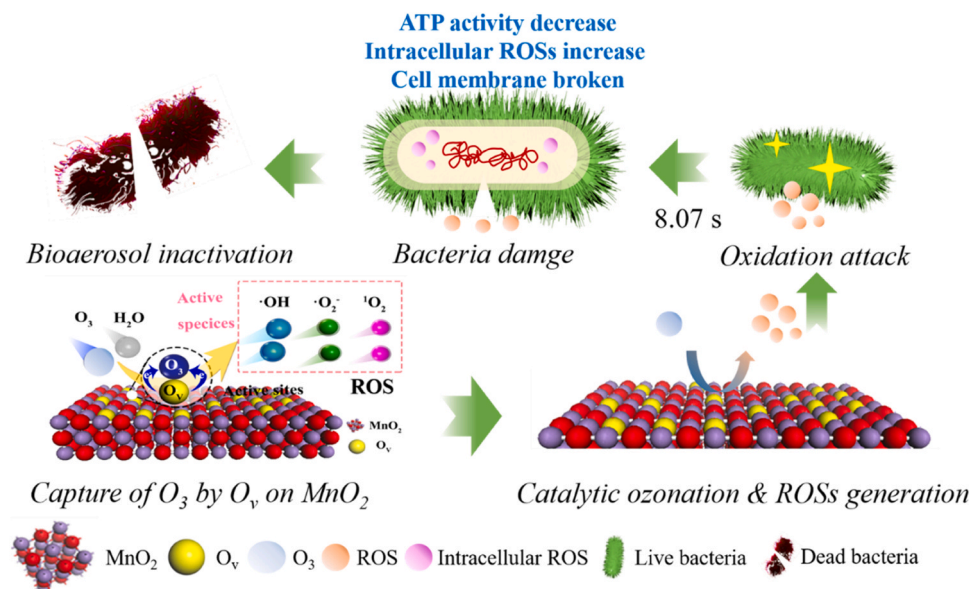


Fig. 6. Illumination of proposed inactivation mechanisms of the MN/O₃ system.

the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123675.

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